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1 Assimilation of sediments embedded in the oceanic arc  
2 crust: myth or reality?

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14 ABSTRACT

15 Arc magmas are commonly assumed to form by melting of sub-arc mantle that has been  
16 variably enriched by a component from the subducted slab. Although most magmas that  
17 reach the surface are not primitive, the impact of assimilation of the arc crust is often  
18 ignored with the consequence that trace element and isotopic compositions are commonly  
19 attributed only to varying contributions from different components present in the mantle.  
20 This jeopardises the integrity of mass balance recycling calculations. Here we use Sr and  
21 O isotope data in minerals from a suite of volcanic rocks from St Lucia, Lesser Antilles  
22 arc, to show that assimilation of oceanic arc basement can be significant. Analysis of  
23  $^{87}\text{Sr}/^{86}\text{Sr}$  in single plagioclase phenocrysts from four Soufrière Volcanic Complex (SVC;  
24 St Lucia) hand samples with similar composition ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7089\text{--}0.7091$ ) reveals  
25 crystal isotopic heterogeneity among hand samples ranging from 0.7083 to 0.7094 with up  
26 to 0.0008 difference within a single hand sample.  $\delta^{18}\text{O}$  measurements in the SVC crystals  
27 show extreme variation beyond the mantle range with +7.5 to +11.1‰ for plagioclase  
28 ( $n=19$ ), +10.6 to +11.8‰ for quartz ( $n=10$ ), +9.4 to +9.8‰ for amphibole ( $n=2$ ) and +9  
29 to +9.5‰ for pyroxene ( $n=3$ ) while older lavas (Pre-Soufrière Volcanic complex), with less  
30 radiogenic whole rock Sr composition ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7041\text{--}0.7062$ ) display values closer to  
31 mantle range: +6.4 to +7.9‰ for plagioclase ( $n=4$ ) and +6 to +6.8‰ for pyroxene ( $n=5$ ).  
32 We argue that the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope disequilibrium and extreme  $\delta^{18}\text{O}$  values provide  
33 compelling evidence for assimilation of material located within the arc crust. Positive  
34 correlations between mineral  $\delta^{18}\text{O}$  and whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  and  
35  $^{206,207,208}\text{Pb}/^{204}\text{Pb}$  shows that assimilation seems to be responsible not only for the isotopic  
36 heterogeneity observed in St Lucia but also in the whole Lesser Antilles since St Lucia

37 encompasses almost the whole-arc range of isotopic compositions. This highlights the need  
38 for detailed mineral-scale investigation of oceanic arc suites to quantify assimilation that  
39 could otherwise lead to misinterpretation of source composition and subduction processes.

## 1.Introduction

A key question in oceanic arc geochemistry concerns the relative contributions of subducting slab and intra-crustal material in the chemical and isotopic characteristics of lavas. Oceanic arc magmas are generated by partial melting of the mantle wedge modified by H<sub>2</sub>O-rich fluids and melts from the subducting slab (Tatsumi and Eggins, 1995) and subsequently ascend through the arc crust before eruption. Lavas erupted at oceanic arcs rarely have major element compositions in equilibrium with mantle peridotite (Annen et al., 2006) which suggests that the magmas experienced differentiation during storage within or at the base of the arc crust. Depending on the nature of the arc basement, such magmas may interact with igneous or metasedimentary wall rocks during differentiation. Distinguishing between sediment addition to the mantle wedge and assimilation of metasediments located in the arc crust is not straightforward on the basis of whole rock compositions alone— the effects of mixing sediment into the mantle wedge or with basaltic melts in the crust are similar in most radiogenic isotope-isotope spaces.

In order to investigate the role of crustal assimilation in oceanic arcs we selected a suite of rocks from the Lesser Antilles arc where, despite the absence of continental basement, whole rock isotope ratios of arc lavas can be very “continental”. As a result, the case has long been made both for crustal assimilation (e.g. Davidson, 1987; Davidson and Harmon, 1989; Smith et al., 1996; Thirlwall et al., 1996; Thirlwall and Graham, 1984; Van Soest et al., 2002), and incorporation of sediment or sediment melt into the mantle wedge (e.g. Carpentier et al., 2008; 2009; Labanieh et al., 2010; 2012; White and Dupré, 1986). Our suite of samples, from the island of St Lucia, encompasses almost the entire range of whole rock isotopic compositions observed in the Lesser Antilles, ranging from values close to

typical intra-oceanic arc rocks to those resembling continental crust (e.g.  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  ranging from 0.70411-0.70906, 0.51210-0.51298 and 19.291-19.797 respectively).  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{18}\text{O}$  analyses of individual minerals separated from lavas with extreme crust-like whole rock isotopic composition from the Soufriere Volcanic Complex (SVC), demonstrate the importance of open system behaviour on oceanic arc magmatism and challenge our understanding of magma differentiation in oceanic arcs.

## **2.Geological background**

The Lesser Antilles arc (Fig. 1) formed as a result of subduction of the North American Plate under the Caribbean Plate. Its lavas have typical oceanic arc compositions in the northern section but unusually heterogeneous isotopic signatures in the central and southern part of the arc where both typical intra-oceanic arc and very continental crust-like signatures are observed (e.g. Macdonald et al., 2000; Fig.2). Two main processes have been proposed to explain these extreme compositions: (1) incorporation of sediment into the mantle source or (2) significant assimilation of sediment-rich arc crust. While a high sediment input to the source could be explained by the presence of abundant sediment in the southern Antilles Trench, due to discharge from the Orinoco and Amazon rivers (e.g. Carpentier et al., 2008; 2009), assimilation of sediment in the arc crust is also possible because the central-southern Lesser Antilles arc is thought to have developed above the thick forearc basin of the (now extinct) Aves Ridge Arc, splitting it into the Grenada and the Tobago basins (Fig. 1; Aitken et al., 2011). Sediments entering the subduction zone are chemically and isotopically well constrained by analyses from DSDP Sites 144 and 543 (Fig.1; Carpentier et al., 2008; 2009; White and Dupré, 1986). In contrast, the nature of the basement of the Southern Lesser Antilles arc is still poorly known. While the detrital

sediments from the South American craton, which dominate the sequences on both the subducting and the overriding plates, were often targeted in the past to explain the high  $^{87}\text{Sr}/^{86}\text{Sr}$  and low  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of the lavas, they fail to explain their very radiogenic Pb signatures. Recently, analyses of Mesozoic black shales sampled at DSDP site 144 showed that these sediments have sufficiently radiogenic Pb to account for the compositions of the lavas from the southern arc (Carpentier et al., 2009). Because such radiogenic Pb has not yet been reported from the sediments of the Grenada and Tobago basins, sediment addition to the source alone has been suggested to explain the whole range of isotopic data in the southern arc lavas (Carpentier et al., 2008; 2009; Labanieh et al., 2010). However, it cannot be ruled out that such sediments exist within the basement of the southern arc since biogenic rich limestones have been reported in the overriding plate, in the Late Cretaceous to Oligocene sequences of the Carupano Basin (Ysaccis, 1997).

St Lucia is an island in the central-southern part of the arc (Fig.1). The lavas from this single island encompass almost the whole range of isotopic variation observed in the arc making it the perfect location to study the influence of crustal components (Fig.2). The more continental crust-like compositions are found in andesites (3Ma to ca. 250 ka) and dacites (100 ka to present) of the Soufriere Volcanic Complex (SVC), while more mantle-like compositions are observed in the more mafic Pre-SVC lavas dominated by basalt, basaltic andesite and andesite (18 Ma to 1.1 Ma; Briden et al., 1979; De Kerneison et al., 1983; Lindsay et al., 2013; Samper et al., 2008; Schmidt et al., 2010).

### **3.Methods**

#### *3.1. Whole rock Sr, Nd and Pb isotopes*

109 Except for 7 samples in which Sr and Nd isotope ratios were measured at the Geochemical  
110 Analysis Unit at Macquarie University (Aus), whole rock powders were analysed at the  
111 Arthur Holmes Isotope Geology Laboratory (AHIGL) which is part of Durham  
112 Geochemistry Centre (DGC) at Durham University (UK) At both institutes, 0.1 g of sample  
113 powder was dissolved in Teflon distilled 29M HF and 16M HNO<sub>3</sub>.

114 At Durham, Pb and Sr were separated from the sample solution using Sr-spec resin  
115 columns. Nd was collected from the same Sr-spec column before being passed through a  
116 cation column where it was collected as part of a total REE cut after elution of Hf, Rb and  
117 Ba. Samples were analysed for their <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb and  
118 <sup>208</sup>Pb/<sup>204</sup>Pb compositions by plasma ionisation multicollector mass spectrometry (PIMMS)  
119 using a Thermo Scientific Neptune instrument. During the <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd  
120 analytical sessions, instrument performance was monitored by analysis of NBS987 Sr  
121 standard and an in house J&M Nd standards and within-run instrument mass fractionation  
122 was corrected using an exponential law and the normalising value of <sup>88</sup>Sr/<sup>86</sup>Sr = 8.375209  
123 and <sup>146</sup>Nd/<sup>145</sup>Nd = 2.079143 respectively (equivalent to <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194 and <sup>146</sup>Nd/<sup>144</sup>Nd  
124 = 0.7219). Since Nd was analysed as part of a total REE cut, the data requires an algebraic  
125 correction for Sm interference on Nd based on the approach of Nowell and Parrish (2001).  
126 The accuracy of this correction was monitored by analysis of Sm-doped J&M, with a  
127 Sm/Nd ratio of ~0.25. The average <sup>87</sup>Sr/<sup>86</sup>Sr for NBS987 was 0.710272 ± 0.000020 (2sd;  
128 n=14) and the average <sup>143</sup>Nd/<sup>144</sup>Nd for both pure and Sm-doped J&M was 0.511105 ±  
129 0.00002 (2sd; n=15). <sup>87</sup>Sr/<sup>86</sup>Sr ratios are reported relative to NBS987 standard value of  
130 0.71024 (Thirlwall, 1991) and <sup>143</sup>Nd/<sup>144</sup>Nd is reported relative to a J&M standard value of  
131 0.511110 which is equivalent to a La Jolla value of 0.511862 (Royse et al., 1998). The



132  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of the two international rock standards BHVO-1 and BIR-  
133 1 were 0.703463 and 0.512989 and 0.703115 and 0.513073 respectively. The accuracy of  
134 the Sm correction on the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio is illustrated by the analysis of BHVO-1, which  
135 after Sm correction is identical to the ratio of  $0.512986 \pm 0.000009$  (2sd; n=19) that Weiss  
136 et al. (2005) obtained by thermal ionisation mass spectrometry (TIMS).

137 Following chemistry, the Pb fractions were taken up in 1 ml of 3%  $\text{HNO}_3$ . The Pb  
138 concentration of the aliquots was analysed before isotopic measurements, in order to  
139 calculate the appropriate amount of Tl spike to add to obtain a Pb/Tl ratio of  $\sim 12$ . This  
140 minimizes the tail from  $^{205}\text{Tl}$  onto  $^{204}\text{Pb}$  and from  $^{206}\text{Pb}$  onto  $^{204}\text{Tl}$ . During isotopic  
141 measurements, the samples were introduced into the Neptune using an ESI PFA50  
142 nebulizer and a cyclonic spray-chamber. The normal H skimmer cone was used. Sensitivity  
143 for Pb on the Neptune using such setup is typically around 100 V total Pb  $\text{ppm}^{-1}$  at an  
144 uptake rate of  $90 \mu\text{m min}^{-1}$ . Pb mass bias was corrected externally using the  $^{205}\text{Tl}/^{203}\text{Tl}$  ratio  
145 of the spike and an exponential law. The  $^{205}\text{Tl}/^{203}\text{Tl}$  used for correction was determined for  
146 each analytical session by minimizing the difference in offset between the session average  
147 Pb ratios and the Galer (1997) triple spike Pb isotope values. The Tl isotope ratio was  
148 calculated to yield the best fit to all the Pb isotope ratios of Galer (1997) simultaneously.  
149 During the analytical sessions, the NBS981 standard solution was analysed regularly  
150 (n=16). The average ratios were:  $^{206}\text{Pb}/^{204}\text{Pb} = 16.941 \pm 0.0024$  (2 sd),  $^{207}\text{Pb}/^{204}\text{Pb} = 15.497$   
151  $\pm 0.0012$  (2 sd),  $^{208}\text{Pb}/^{204}\text{Pb} = 36.715 \pm 0.0039$  (2 sd). Furthermore, a total procedural  
152 BHVO-1 was analysed. The  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios obtained were  
153 18.687, 15.568 and 38.342, respectively which is in good agreement with the GEOREM

accepted value ( $^{206}\text{Pb}/^{204}\text{Pb} = 18.692 \pm 0.008$  (2 sd);  $^{207}\text{Pb}/^{204}\text{Pb} = 15.572 \pm 0.006$  (2 sd);  
 $^{208}\text{Pb}/^{204}\text{Pb} = 38.355 \pm 0.022$  (2 sd)).

At Macquarie, Sr was separated from the sample solution using Biorad AG50W-X8 resin and Nd was collected after separation from Ba and LREE using Eichrom<sup>®</sup> Ln.spec resin columns following the method of Pin et al. (1997).  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were measured by TIMS using a Thermo-Fisher Triton instrument. During the analytical session, instrument performance was monitored by analyses of Sr standards NBS987 and Nd standard JMC321 and mass bias was corrected as in Durham. The average  $^{87}\text{Sr}/^{86}\text{Sr}$  for NBS987 was  $0.710220 \pm 0.000022$  (2sd, n=4) and the average  $^{143}\text{Nd}/^{144}\text{Nd}$  for JMC321 was  $0.511123 \pm 0.000006$  (2sd; n=3).  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  were not reported relative to a literature value. During the course of this study, analyses of processed international BHVO-2 standard yielded average  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of was  $0.703469 \pm 0.000012$  (2sd; n=4) and  $0.512976 \pm 0.000012$  (2sd; n=4), respectively.

### 3.2. $^{87}\text{Sr}/^{86}\text{Sr}$ in plagioclase

Four of the most continental-like lavas from St Lucia (SVC), ranging from andesitic to dacitic in composition and with very similar whole rock radiogenic isotope signatures, were chosen for in-depth isotopic study. Sr isotope ratios were determined for five single plagioclase crystals from each lava. The crystals were carefully hand-picked from lightly crushed hand specimens using a binocular microscope. Grains were selected for being free of both inclusions and adhering glass. Each grain, containing at least 60 ng Sr, was individually digested in Romil Upa grade  $\text{HNO}_3$  and HF. Sr was separated using Sr-spec

resin columns and  $^{87}\text{Sr}/^{86}\text{Sr}$  was measured by TIMS using the Thermo Fisher Triton at Durham University. During the TIMS analyses, the average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for NBS987 obtained on 12ng of Sr was  $0.710243 \pm 0.000009$  (2sd, n=3). This is in excellent agreement with the value reported by Thirlwall (1991) of  $0.710248 \pm 0.000023$  (2sd, n=427). Two total procedure blanks contained 18 and 32 pg of Sr which represent 0.03 and 0.05% of the lowest sample Sr concentration analysed and are therefore negligible.

### *3.3. $\delta^{18}\text{O}$ in mineral separates*

Samples ranging from typical oceanic arc lavas to the most continental-like composition were selected for individual mineral oxygen isotope extraction by laser-fluorination. Minerals separates were hand-picked from lightly crushed hand specimens under a binocular microscope, avoiding any inclusions or glass adhering to the grains. Oxygen was extracted from 0.9-3.7 mg of separate using a total laser fluorination system based on the method of Sharp (1990), at the Scottish Universities Environmental Research Centre (SUERC). All fluorinations resulted in 100% release of  $\text{O}_2$  from mineral lattice. This oxygen was converted to  $\text{CO}_2$  and analyzed on a VG Optima mass spectrometer. Oxygen isotope ( $\delta^{18}\text{O}$ ) values are reported as per mil (‰) deviations relative to Vienna Standard Mean Ocean Water (V-SMOW). Samples were analysed during two periods. During the first period (March 2012) 31 unknowns were analysed along with the international and in-house standards UWG2 and SES and GP147. The average  $\delta^{18}\text{O}$  values obtained for UWG2 (garnet,  $+5.7\text{‰} \pm 0.2$  (2sd), n = 11), SES (quartz,  $+10.4\text{‰} \pm 0.6$  (2sd), n = 10) and GP147 (garnet,  $+7.2\text{‰} \pm 0.4$  (2sd), n = 3) are in very good agreement with their accepted values of  $+5.8\text{‰}$  (Valley et al., 1995),  $+10.2\text{‰}$  and  $+7.2\text{‰}$  (Mattey and Macpherson, 1996) respectively. The internal SES standard has been run many hundreds of time over the past

20 years in SUERC, and is well calibrated against UWG2, NBS 28 and NBS 30, as well as GP147. Twelve unknowns were analysed during the second period of study (November 2012) when the average  $\delta^{18}\text{O}$  values for UWG2, SES and GP147 were  $+5.9\text{‰} \pm 0.2$  (2 sd,  $n = 2$ ),  $+10.2\text{‰} \pm 0.3$  (2 sd,  $n = 6$ ),  $+7.15\text{‰} \pm 0.4$  (2 sd,  $n = 2$ ) respectively.

#### 4.Results

Whole rock Sr, Nd and Pb isotope ratios are given in Table 1. Plagioclase Sr isotopes and mineral  $\delta^{18}\text{O}$  data are presented in Tables 2 and 3 respectively.

Whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios range between 0.70411 and 0.70622 and 0.51251 and 0.51298, respectively, in the Pre-SVC samples and from 0.70754 to 0.70906 and 0.51210 to 0.51226, respectively, in the SVC samples (Fig. 2a). Whole rock  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios were analysed in selected samples with the highest and the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios, to verify coupling with other isotopic systems. Pb isotope ratios vary from 19.291 to 19.341 for  $^{206}\text{Pb}/^{204}\text{Pb}$ , from 15.747 to 15.748 for  $^{207}\text{Pb}/^{204}\text{Pb}$  (Fig. 2b) and from 38.96 to 39.11 for  $^{208}\text{Pb}/^{204}\text{Pb}$  in the Pre-SVC lavas analysed. In the SVC lavas, ratios vary from 19.721 to 19.797 for  $^{206}\text{Pb}/^{204}\text{Pb}$ , from 15.826 to 15.846 for  $^{207}\text{Pb}/^{204}\text{Pb}$  and from 39.438-39.528 for  $^{208}\text{Pb}/^{204}\text{Pb}$ . Plagioclase crystals from the SVC have heterogeneous  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (Fig. 3) ranging between 0.7083 and 0.7094 with variations of up to 0.00083 among crystals from a single lava (SL-JL-51). In the Pre-SVC, plagioclase and pyroxene  $\delta^{18}\text{O}$  vary from + 6.4 to +7.9‰ and from +6 to +6.8‰ respectively (Fig. 4). In the SVC, mineral  $\delta^{18}\text{O}$  are higher and vary from +7.5 to +10.9‰ for plagioclase, from +10.6 to +11.8‰ for quartz, from +9.4 to +9.8‰ for amphibole and +9 to +9.5‰ for pyroxene.

## 5. Discussion

### 5.1. Intra-crustal magma contamination

The unusually radiogenic composition of some lavas from the Lesser Antilles arc has been explored by many authors using whole rock samples, and explained through models invoking either sediment incorporation into the source (e.g. Labanieh et al., 2010) or assimilation during fractional crystallisation (AFC; e.g. Davidson, 1987). Discriminating between these two processes using only whole rock isotopes is difficult mainly due to uncertainties in determining the precise composition of the endmembers. Correlations between whole rock isotopes and indexes of differentiation such as SiO<sub>2</sub> or MgO are however useful in detecting isotopic changes during differentiation and have been employed by several authors to argue for AFC in Grenada (Thirlwall et al., 1996), the Grenadine Islands (Smith et al., 1996) and Martinique (Davidson, 1987; Davidson and Wilson, 2011). In St Lucia, two distinct trends are observed (Fig. 2c): the first one, comprising only some Pre-SVC samples (Pre-SVC1), shows an absence of covariation between radiogenic isotopes and SiO<sub>2</sub> or MgO while the second trend, comprising the remaining Pre-SVC (Pre-SVC2) and the SVC lavas, displays progressive increase in Sr and decrease in Nd isotope ratios with increasing SiO<sub>2</sub> and decreasing MgO. Pb isotope ratios were not analysed for all St Lucia lavas but variations in the Pre-SVC1 and SVC lavas are consistent with those defined by Sr and Nd isotopes (Fig. 2d). While the first (“vertical”) trend can be explained by simple differentiation of a mafic mantle-derived magma, the second trend requires a different/additional process. If this latter trend were to reflect a source process, this would require either (1) the production of silicic SVC magmas in the mantle or (2) their derivation by differentiation of more mafic melts from a mantle

source where a common factor controls both the amount of sediment melt/sediment derived fluids added to the source and the future extent of magma differentiation. The first hypothesis cannot be reconciled with the low MgO content of silicic SVC lavas compositions (MgO = 1.1-2.7 wt.%) since andesitic to dacitic magma generated either by mantle melting or by reaction between ascending slab-derived silicic melts and mantle peridotite typically have elevated MgO contents (Grove et al., 2003; Yogodzinsky and Kelemen, 1998). The second hypothesis, involving a coincidental process, is equally very hard to conceive. It is, however, directly testable. Since magmatic differentiation has negligible effect on radiogenic isotopic ratios, the amount of sediment incorporated into the magma during its genesis in the mantle should be reflected in the  $^{87}\text{Sr}/^{86}\text{Sr}$  of all its components. Therefore, once separated from its source, a magma that has remained a closed system should demonstrate negligible  $^{87}\text{Sr}/^{86}\text{Sr}$  variation between the melt and all phenocrysts. Furthermore, the Sr isotope ratio of the phenocrysts would also be observed for the whole rock. Conversely, isotopic disequilibrium between different phases in a rock or between different crystals of the same phase would require that open system behaviour occurred. Therefore, the variation in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios within single samples is a hallmark for open system behaviour (Davidson et al., 2007).

Despite their similar whole rock Sr isotopic ratios, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of crystals from the four SVC samples vary substantially amongst and within hand specimens (Table 2; Fig.3). Such disequilibrium cannot be explained by incorporation of sediment in the source, and must instead be accounted for by an open system process, such as crustal assimilation during crystallisation.

Most of the plagioclase crystals analysed have lower  $^{87}\text{Sr}/^{86}\text{Sr}$  than their respective whole rock values. This indicates that at least part of the volume of each of those plagioclase crystals grew in a magma with less radiogenic Sr than now represented by the matrix. The zoned nature of the crystals requires an igneous origin but does not allow discrimination between phenocrysts which grew from a magma changing in  $^{87}\text{Sr}/^{86}\text{Sr}$  composition and xenocrysts which were remobilized during re-melting of plutonic rocks. The latter option was preferred by Schmitt et al. (2010) to explain variation in core to rim U-Th zircon ages obtained in the SVC lavas.

## *5.2. Effect of contamination on whole rock compositions*

In order to confirm that crustal assimilation is largely responsible for the radiogenic whole rock isotopic signatures observed in St Lucia, the mineral  $\delta^{18}\text{O}$  study was performed. Although the  $\delta^{18}\text{O}$  of crustal-derived material ( $> +10\text{‰}$ ) is much higher than the mantle range ( $+ 5.5\text{‰} \pm 0.2$ ), 80% of the  $\delta^{18}\text{O}$  values of any given phase in oceanic arc lavas fall within  $\pm 0.2\text{‰}$  of the average value for that phase in upper mantle peridotites and MORBs (Eiler et al., 2000; Matthey et al., 1994). Because the concentration of oxygen in the mantle and the crust is similar, a large input of crustal derived fluids and/or sediments would be necessary to modify the mantle signature (James, 1981). Thus, O isotopes provide a powerful tool to discriminate between addition of sediments to the mantle source from assimilation of sediments in the arc crust, the latter being a much more efficient way of modifying the mantle-derived  $\delta^{18}\text{O}$  value of the magma (e.g. Macpherson et al., 1998). Previous oxygen isotopic analyses performed on olivine and pyroxene phenocrysts from the Lesser Antilles showed the existence of values greater than the mantle range and that

these correlate with whole rock radiogenic isotopes, suggesting crustal assimilation (Smith et al., 1996; Thirlwall et al., 1996; Van Soest et al., 2002). However, although higher, the excess relative to the range of mantle  $\delta^{18}\text{O}$  values was small, with only up to + 1‰ excess for olivine and up to + 0.6‰ for pyroxene with the exception of one pyroxene, which was + 1.6‰ and two quartz crystals which were + 3.83‰ and + 4.37‰ higher than the mantle range.

In this study, 93% of the 44 mineral analyses lie outside their respective mantle ranges and the SVC displays extreme  $\delta^{18}\text{O}$  values never observed before in oceanic arcs lacking known continental basement (Fig.4). Moreover, a strong positive correlation is observed between the mineral  $\delta^{18}\text{O}$  and the whole rock radiogenic isotopes (Fig. 5) with the highest  $\delta^{18}\text{O}$  values found in SVC lavas with very radiogenic whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{206,207,208}\text{Pb}/^{204}\text{Pb}$  ratios (and unradiogenic  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios). Although the SVC products have more differentiated compositions than the pre-SVC samples, the maximum effect of closed system differentiation on  $\delta^{18}\text{O}$  is typically very small: +0.3 to +0.4‰ (Bindeman et al., 2004; Macpherson and Matthey, 1998). Thus, even after correction for this effect, the SVC mineral  $\delta^{18}\text{O}$  range lies well beyond the mantle range. The mean anorthite (An) content of SVC plagioclase is slightly lower than that of the pre-SVC crystals. However, since the difference is small (mean An of 68% (ranging from 65% to 71%) and of 59% (ranging from 54% to 68%) respectively for SVC andesite and dacite vs. mean An of 80% (70% - 90%) for Pre-SVC basaltic andesite and basalt) the related increase in  $\delta^{18}\text{O}$  in the SVC plagioclase is thought to be negligible. This is confirmed by the fact that phenocrysts from SVC lavas with different  $\text{SiO}_2$  (high-silica andesites and dacites: 60.5 – 67.5 wt. %) possess similar  $\delta^{18}\text{O}$  values. SVC plagioclase-quartz pairs (from the same hand sample)



311 have  $\Delta_{\text{plag-qtz}}$  (where  $\Delta_{i-j} = \delta^{18}\text{O}_i - \delta^{18}\text{O}_j$ ) between -0.1 to -1.21 ‰ (n = 8; with n=5 higher  
 312 than -0.7‰) except for one pair where  $\Delta_{\text{plag-qtz}} = -3.9$  ‰. Andesitic-dacitic temperatures  
 313 (T= 800-1000°C) typically produce  $\Delta_{\text{plag-qtz}}$  between -0.84 and -1.45 ‰ (e.g. using the  
 314 Chiba et al. (1989) fractionation coefficients and considering a large range of anorthite  
 315 content between An<sub>40</sub> and An<sub>70</sub>). Therefore, most  $\Delta_{\text{plag-qtz}}$  are higher than equilibrium. SVC  
 316 plagioclase-pyroxene pairs display fractionation of  $\Delta_{\text{plag-py}}$  between +0.60 and +0.95 ‰  
 317 (n=3) which are similar to that expected from equilibrium fractionation at andesitic-dacitic  
 318 temperatures ( $\Delta_{\text{plag-py}} = +0.66$  to  $+1.21$  ‰ at T° = 800-1000 and An<sub>40-70</sub>). Therefore, both  
 319 pyroxene and plagioclase are likely to have crystallized in equilibrium from a similar  
 320 magma. The lowest  $\delta^{18}\text{O}$  values are observed in Pre-SVC1 lavas, which have low whole  
 321 rock  $^{87}\text{Sr}/^{86}\text{Sr}$  and Pb isotope ratios (SL-83-25, 44). In these samples,  $\delta^{18}\text{O}_{\text{plag}}$  values are  
 322 higher than the mantle range, whereas the  $\delta^{18}\text{O}_{\text{px}}$  values overlap the upper end of the mantle  
 323 range. However, plagioclase-pyroxene pairs ( $\Delta_{\text{plag-py}}$  from +0.3 to +0.6 ‰) are close to  
 324 oxygen isotopic equilibrium at basaltic to basaltic andesite temperatures ( $\Delta_{\text{plag-py}} = +0.35$   
 325 ‰ to +0.51‰ at T° = 1100-1200°C and An<sub>99-80</sub> using Chiba et al.'s (1989) equation). Thus,  
 326 it is difficult, in these samples, to differentiate between small error on the mantle mineral  
 327 range of composition and the impact of small amounts of crustal assimilation during  
 328 plagioclase crystallization. Pre-SVC2 lavas, that have the highest whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$   
 329 ratios (SL-83-26;  $^{87}\text{Sr}/^{86}\text{Sr} = 0.706219$ ; basaltic andesite) of the Pre-SVC group, also  
 330 display higher  $\delta^{18}\text{O}_{\text{plag}}$  than  $\delta^{18}\text{O}_{\text{px}}$ . However,  $\Delta_{\text{plag-py}}$  varies between +0.5 ‰ to +1.5 ‰.  
 331 Such values are too high to be explained simply by equilibrium fractionation. We believe  
 332 that the high  $\Delta_{\text{plag-py}}$  values result from the addition of a crustal component late in the  
 333 differentiation sequence when plagioclase formed a larger component of the crystallising

334 assemblage. This provides further support for an origin through crustal assimilation rather  
335 than sediment addition to the source. In this case, plagioclase provides a more sensitive  
336 record of crustal assimilation than the mafic phases. This may be important when targeting  
337 minerals for oxygen isotopic analysis in settings where more subtle changes in  $\delta^{18}\text{O}$  are  
338 anticipated, due to smaller isotopic contrasts between magma and the crust into which it is  
339 emplaced.

340 A simple mixing model (Fig. 5) between a typical mantle composition and a sediment  
341 having the highest  $\delta^{18}\text{O}$  reported (+ 35 ‰; Bindeman, 2008) shows that a minimum of 10-  
342 20 % of sediment would be required to be added to the mantle or a mantle derived magma  
343 in order to explain the SVC mineral  $\delta^{18}\text{O}$  data. However, we know from DSDP 78A site  
344 543 and DSDP 14 site 144 that sediments subducted at the Lesser Antilles trench comprise  
345 a mixture of pelagic clay, radiolarian clay, terrigenous claystone siltstone and sandstones  
346 (30% carbonate on average; Carpentier et al., 2008). Thus, the bulk sediment would possess  
347 an average  $\delta^{18}\text{O}$  closer to the composition of site 543 pelagic clays of +20‰ (Davidson,  
348 1987). In this more realistic case, addition of 20-40% sediment would be required to  
349 generate the range of SVC  $\delta^{18}\text{O}$  values and addition of 10-20% sediment could reproduce  
350 the Pre-SVC sample with the most elevated  $\delta^{18}\text{O}_{\text{plag}}$  (+7.3 to +7.9‰ in SL-83-26; Fig. 5c).  
351 Introducing such large amounts of sediments to the mantle wedge should also modify the  
352 major element composition of the primitive magmas, such that increasing sediment  
353 incorporation (i.e. increasing mineral  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) should correlate with an increase  
354 of  $\text{SiO}_2$  (clay, sand) or  $\text{CaO}$  (carbonate) of the melt. As discussed in section 5.1., the SVC  
355 lavas cannot have been directly produced in the mantle since their  $\text{MgO}$  is too low. If the  
356 SVC lavas resulted from differentiation of a primary magma produced in the mantle by

mixing with substantial amounts of sediment melt, the resulting suite of lava would likely have a higher SiO<sub>2</sub> or CaO content than a suite derived from Pre-SVC<sub>1,2</sub> primitive magmas at a given MgO content (different differentiation trends). However, SVC and Pre-SVC<sub>1,2</sub> lavas share similar (although scattered) differentiation trend (Fig. 6), and therefore back project toward a similar primitive magma. Hence, it seems unlikely that the SVC and Pre-SVC lavas were derived from very different mantle sources. Instead, the single trend of differentiation recorded by major elements in all St Lucia lavas is consistent with variable assimilation of crustal material. This is because, during differentiation, major element compositions are largely controlled by phase equilibria and, to a lesser extent, by the nature of the sediment assimilated, the latter likely to be derived from the erosion of upper continental crust with a similar composition to the felsic differentiates of the Pre-SVC lavas (Fig. 6). Therefore, the strong correlation between  $\delta^{18}\text{O}$  and whole rock Sr isotopes indicate that assimilation is the major factor controlling the whole rock radiogenic isotope ratios observed in the St Lucia lavas (Fig.7). For both plagioclase and pyroxene, the correlation is slightly convex-up, suggesting that the magma had a slightly lower Sr content than the material it assimilated (c.f. inset to Fig.5). More importantly, the plagioclase  $\delta^{18}\text{O}$  values are displaced further from the mantle field than is the case for pyroxene in Pre-SVC samples, requiring a larger proportion of assimilant than required for the pyroxenes. Quartz is only found in the SVC lavas where no correlation between  $\delta^{18}\text{O}_{\text{qz}}$  and whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$  is observed. The slight disequilibrium between quartz and plagioclase (low  $\Delta_{\text{plag-qtz}}$ ) indicates that quartz crystallized in a magma with slightly lower  $\delta^{18}\text{O}$  than the plagioclase.

### 5.3. Implications for other Lesser Antilles volcanoes and other arcs

The crystal  $^{87}\text{Sr}/^{86}\text{Sr}$  data show that lavas with extreme whole rock compositions underwent assimilation of crustal material in an open system supporting previous work by Davidson (1987), Davidson and Harmon (1989) Smith et al. (1996), Thirwall et al. (1996), Thirlwall and Graham (1984) and Van Soest et al. (2002). The extreme  $\delta^{18}\text{O}$  signature observed in lavas with the most continental Sr, Nd and Pb isotope ratios (SVC) confirms late assimilation of arc crust as the cause of these variations and shows that the amount of material assimilated is not trivial ( $>20\%$ ). More importantly, crustal assimilation did not only affect the andesites and dacites, but also substantially (10-20% assimilation) modified the composition of a basaltic andesite (Pre-SVC2) with similar  $\text{SiO}_2$  and  $\text{MgO}$  contents to the most mafic lava of the island. Therefore, in St Lucia, the use of the most mafic lavas erupted on the island to constrain the source characteristics is compromised since some of them have clearly interacted with the crust. Similar problems may affect other Lesser Antilles islands and other oceanic arcs where basaltic andesites with  $\text{MgO} \sim 4 \text{ wt. } \%$ , or even more differentiated lavas, have been used studies to constrain the source composition. For example Labanieh et al. (2010) suggested that isotopic ratios in lavas from Martinique with up to  $\sim 70 \text{ wt. } \%$   $\text{SiO}_2$  ( $\text{MgO} \sim 0.23$ ) faithfully reflect the source composition. Likewise, Carpentier et al. (2008) modeled all the published data for Lesser Antilles lavas by sediment addition to the source, without taking into account the degree of differentiation of the lavas.

Because St Lucia lavas encompass Sr, Nd and Pb isotopic range almost as great as the whole Lesser Antilles arc it follows that much of the isotopic heterogeneity observed in the rest of the arc could also reflect variable crustal assimilation. Sediment present in the Lesser Antilles arc crust is likely to originate from the closest continental mass: South America.

It has very “continental”  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{206,207,208}\text{Pb}/^{204}\text{Pb}$  ratios (e.g. Carpentier et al., 2008). Sediments with such signatures were found on the edge of the north east part of South America (site 144 sediment; Carpentier et al.(2008, 2009)) and their presence on the subducting plate was used as a strong argument for incorporation of sediment in the mantle source as being the cause for the extreme isotopic compositions of the arc lavas. However, our data show that most of the arc lava isotopic variations are generated by contamination in the arc crust. Therefore, subduction of material resembling site 144 sediments is not *required* to explain the extreme Sr, Nd, Pb and O isotopic signatures of the Lesser Antilles arc lavas.

It is important to stress that this does not preclude incorporation of subducted sediment into the source of the lavas having an impact on the whole rock isotopic ratios. Indeed, mineral  $\delta^{18}\text{O}$  compositions of the Pre-SVC1 lavas (SL-83-44; SL-83-25) are very close to mantle values which indicate that, if crustal assimilation affected these lavas, it would be in very low amounts. Yet, although their Sr and Nd isotope ratio overlap typical oceanic arc compositions, their Pb isotope ratios are slightly more radiogenic (Fig. 2b). This not only suggests the involvement of sediment in the source but also that these are slightly more abundant or more radiogenic than sediments present in the source of most “typical” oceanic arcs. However, Sr, Nd and Pb isotope compositions of the Pre-SVC1 lavas remain very close to typical oceanic composition spectrum, and we suggest that subducted material is not a major factor in causing large isotopic heterogeneity in Lesser Antilles arc lavas.

The extreme contamination observed in at least some of the Lesser Antilles lavas may reflect the unique presence of sediment in the arc crust that, in turn, reflects a specific geodynamic context (Aitken et al., 2011). However, similar assimilation of sediments and/or altered crust in lower amounts and/or different composition may occur in other oceanic arcs and has already been suggested to explain compositions observed in the offshore Taupo Volcanic zone in New Zealand (Macpherson et al., 1998). Eiler et al. (2000) estimated that although most oceanic arc minerals (olivine, plagioclase, glass, biotite) fall within the mantle range in  $\delta^{18}\text{O}$ , around 20% of the data are slightly higher by up to 0.43‰. These 'out of mantle range' phases come from samples with higher whole rock Sr isotope ratios, which is also what we observe on St Lucia. Because the displacement from the mantle range is not substantial, these data have been interpreted to reflect sediment incorporation into the mantle wedge. However, all these higher  $\delta^{18}\text{O}$  ratios were observed in mafic minerals (primarily olivine). At St Lucia, in the least contaminated rocks, plagioclase reveals assimilation more clearly than pyroxene, probably because it crystallised over a greater range of magmatic evolution, persisting to the most differentiated stages. Hence, comparing olivine and pyroxene  $\delta^{18}\text{O}$  values with whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$  may be a less effective means to detect small amounts of assimilation than the use of plagioclase  $\delta^{18}\text{O}$  data.

## **6. Summary and conclusions**

Our new single plagioclase Sr isotopic data and mineral  $\delta^{18}\text{O}$  data show that crustal assimilation was important in magma evolution at St Lucia. Correlations of mineral  $\delta^{18}\text{O}$  values with whole rock Sr isotopic composition shows that assimilation controls most of the Sr, Nd and Pb isotopic variation in St Lucia lavas. Isotopic variation at St. Lucia

replicates most of the range for the whole Lesser Antilles arc, therefore we suggest that up to 20-40% assimilation could be responsible for the unusual diversity of isotopic compositions observed along the arc. Assimilation of such large volumes of sediment within the Lesser Antilles crust may be related to a specific geographic and geodynamic setting. However, similar crustal assimilation could take place in other oceanic arcs where a lack of geochemical contrast between assimilated sediments and the magma and/or the lower amounts of sediments assimilated may make it more challenging to track.

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#### **References**

- Annen, C., Blundy, J.D. and Sparks, R.S.J., 2006. The Genesis of Intermediate and silicic magmas in deep crustal hot zones. *J. Petrology* 47, 505-539.
- Aitken, T., Mann, P., Escalona, A., Christeson, G.L., 2011. Evolution of the Grenada and Tobago Basins and implications for arc migration. *Mar. Petrol. Geol.* 28, 235-258.

468 Bindeman, I., 2008. Oxygen Isotopes in Mantle and Crustal Magmas as Revealed by Single  
469 Crystal Analysis. *Rev. Mineral. Geochem.* 69, 445-478.

470 Bindeman, I.N., Valley, J.W., 2002. Oxygen isotope study of the Long Valley magma  
471 system, California: isotope thermometry and convection in large silicic magma bodies.  
472 *Contrib. Mineral. Petrol.* 144, 185-205.

473 Bindeman, I.N., Ponomareva, V.V., Bailey, J.C., Valley, J.W., 2004. Volcanic arc of  
474 Kamchatka: a province with high- $\delta^{18}\text{O}$  magma sources and large-scale  $^{18}\text{O}/^{16}\text{O}$  depletion  
475 of the upper crust. *Geochim. Cosmochim. Acta* 68, 841-865.

476 Briden, J.C., Rex, D.C., Faller, A.M., Tomblin, J.F., 1979. K-Ar geochronology and  
477 paleomagnetism of volcanic rocks in the Lesser Antilles island arc. *Philos. Trans. R. Soc.*  
478 *Lond. A Math. Phys. Eng. Sci.* 291, 485-528.

479 Carpentier, M., Chauvel, C., Mattielli, N., 2008. Pb–Nd isotopic constraints on  
480 sedimentary input into the Lesser Antilles arc system. *Earth Planet. Sci. Lett.* 272, 199-  
481 211.

482 Carpentier, M., Chauvel, C., Maury, R.C., Mattielli, N., 2009. The ‘Zircon effect’ as  
483 recorded by the chemical and Hf isotopic composition of Lesser Antilles forearc sediments.  
484 *Earth Planet. Sci. Lett.* 287, 86-99.

485 Chazot, G., Lowry, D., Menzies, M., Matthey, D., 1997. Oxygen isotopic composition of  
486 hydrous and anhydrous mantle peridotites. *Geochim. Cosmochim. Acta* 61, 161-169.



487 Chiba, H., Chacko, T., Clayton, R.N., Goldsmith, J.R., 1989. Oxygen isotope fractionations  
488 involving diopside, forsterite, magnetite, and calcite: Application to geothermometry.  
489 *Geochim. Cosmochim. Acta* 53, 2985-2995.

490 Davidson, J. P., 1986. Isotopic and trace element constraints on the petrogenesis of  
491 subduction-related lavas from Martinique, Lesser Antilles. *J. Geophys. Res.* 91, 5943-  
492 5962.

493 Davidson, J.P., 1987. Crustal contamination versus subduction zone enrichment: example  
494 from the lesser antilles and implications for mantle source compositions of island arc  
495 volcanic rocks. *Geochim. Cosmochim. Acta* 51, 2185-2198.

496 Davidson, J.P., Harmon, R.S., 1989. Oxygen isotope constraints on the petrogenesis of  
497 volcanic arc magmas from Martinique, Lesser Antilles. *Earth Planet. Sci. Lett.* 95, 255-  
498 270.

499 Davidson, J.P., Morgan, D.J., Charlier, B.L.A., Harlou, R., Hora, J. M., 2007.  
500 Microsampling and isotopic analysis of igneous rocks: implications for the study of  
501 magmatic systems. *Annu. Rev. Earth Planet. Sci.* 35, 273-311.

502 Davidson, J.P., Wilson, M., 2011. Differentiation and Source Processes at Mt Pelée and  
503 the Quill; Active Volcanoes in the Lesser Antilles Arc. *J. petrology* 52, 1493-1531.

504 De Kerneizon, M.L., Bellon, H., Carron, J.P., Maury, R.C., 1983. The island of St-Lucia-  
505 petrochemistry and geochronology of the main magmatic series. *Bull. Soc. Géol. Fr.* 25,  
506 845-853.

507 Eiler, M.J., Crawford, A., Elliott, K.A.F., Valley, J.W. and Stolper, E.M., 2000. Oxygen  
508 Isotope Geochemistry of Oceanic-Arc Lavas. *J. petrology* 41, 229-256.

509 Grove, T.L., Elkins-Tanton, L.T., Parman, S.W., Chatterjee, N., Muntener, O., Gaetani,  
510 G.A., 2003. Fractional crystallisation and mantle melting controls on calc-alkaline  
511 differentiation trends. *Contrib. Mineral. Petrol.* 145, 515-533.

512 James, D.E., 1981. The combined use of oxygen and radiogenic isotopes as indicators of  
513 crustal contamination. *Annu. Rev. Earth Planet. Sci.* 9, 311-344.

514 Heath, E., Macdonald, R., Belkin, H., Hawkesworth, C., Sigurdsson, H., 1998.  
515 Magmagenesis at Soufriere Volcano, Lesser Antilles Arc. *J. Petrology* 39, 1721-1764.

516 Labanieh, S., Chauvel, C., Germa, A., Quidelleur X., Lewin E., 2010. Isotopic hyperbolas  
517 constrain sources and processes under the Lesser Antilles arc. *Earth Planet. Sci. Lett.* 298,  
518 35-46.

519 Labanieh, S., Chauvel, C., Germa, A., Quidelleur, X., 2012. Martinique: a clear case for  
520 sediment melting and slab dehydration as a function of distance to the trench. *J. Petrology*  
521 53, 2441-2464.

522 Lindsay, J.M., Trumbull, R.B., Schmitt, A.K., Stockli, D.F., Shane, P., Howe, T., 2013.  
523 Volcanic stratigraphy and geochemistry of the Soufrière Volcanic Center, Saint Lucia with  
524 implications for volcanic hazards. *J. Volcanol. Geoth. Res.* doi:  
525 10.1016/j.jvolgeores.2013.04.011.

526 Macdonald, R., Hawkesworth, C.J., Heath, E., 2000. The Lesser Antilles volcanic chain: a  
527 study in arc magmatism. *Earth-Sci. Rev.* 49, 1-76.

528 Macpherson, C.G., Matthey, D.P., 1998. Oxygen isotope variations in Lau Basin basalts.  
529 Chem. Geol. 144, 177-194.

530 Macpherson, C.G., Gamble, J.A., Matthey, D.P., 1998. Oxygen isotope geochemistry of lavas  
531 from an oceanic to continental arc transition, kermadec-Hikurangi margin, SW pacific.  
532 Earth Planet. Sci. Lett. 160, 609-620.

533 Matthey, D.P., Macpherson, C., 1993. High-precision oxygen isotope microanalysis of  
534 ferromagnesian minerals by laser fluorination. Chem. Geol., 105, 305-318.

535 Matthey, D.P., Lowry, D., Macpherson, C., 1994. Oxygen isotope composition of mantle  
536 peridotite. Earth Planet. Sci. Lett. 128, 231-241.

537 Nowell, G., Parrish, R.R., 2001. Simultaneous acquisition of isotope compositions and  
538 parent/daughter ratios by non-isotope dilution solution-mode plasma ionisation multi-  
539 collector mass spectrometry (PIMMS). In: Plasma Source Mass Spectrometry: The New  
540 Millennium. Roy. Geol. Soc. Lond. 267, 305 pp.

541 O'Neil, J.R., Chappell, B.W., 1977. Oxygen and hydrogen isotope relations in the Berridale  
542 batholiths. J. Geol. Soc. 133, 559-571.

543 Pin, C., Francisco, J., Zalduegui, S. 1997. Sequential separation of light rare-earth  
544 elements, thorium and uranium by miniaturized extraction chromatography: Application  
545 to isotopic analyses of silicate rocks. Anal. Chim. Acta 339, 79-89.

546 Royse, K., Kempton, P., Darbyshire, D.P.F. 1998. Procedure for the analysis for Rubidium-  
547 Strontium and Samarium-Neodymium isotopes at the NERC Isotope Geosciences  
548 Laboratory. NERC Isot. Geosc. Lab. Rep. Series 121.

549 Samper, A., Quidelleur, X., Boudon, G., Le Friant, A., Komorowski, J.C., 2008.  
 550 Radiometric dating of three large volume flank collapses in the Lesser Antilles Arc. J.  
 551 Volcanol. Geoth. Res. 176, 485-492.

552 Schmitt, A.K., Stockli, D.F., Lindsay, J.M., Robertson, R., Lovera, O.M., Kislitsyn, R.,  
 553 2010. Episodic growth and homogenization of plutonic roots in arc volcanoes from  
 554 combined U-Th and (U-Th)/He zircon dating. Earth Planet. Sci. Lett. 295, 91-103.

555 Sharp, Z.D., 1990. A laser-based microanalytical method for the in situ determination of  
 556 oxygen isotope ratios in silicates and oxides. Geochim. Cosmochim. Acta 54, 1353-1357.

557 Sherman, S.B., 1992. Geochemistry and petrogenesis of Saba, Lesser Antilles, [MSc.  
 558 thesis]. University of South Florida, Tampa. 114 pp.

559 Smith, T.E., Thirlwall, M.F., Macpherson, C., 1996. Trace element and isotope  
 560 geochemistry of the volcanic rocks of Bequia, Grenadine Island, Lesser Antilles Arc: a  
 561 study of subduction enrichment and intra-crustal contamination. J. Petrology 37, 117-143.

562 Tatsumi, Y., Eggins, S., 1995. Subduction Zone Magmatism. Oxford: Blackwell Scientific.

563 Thirlwall, M.F., 1991. Long-term reproducibility of multicollector Sr and Nd isotope ratio  
 564 analysis. Chem. Geol. 94, 85-104.

565 Thirlwall, M. F., Graham, A. M., 1984. Evolution of high-Ca, high-Sr C-series basalts from  
 566 Grenada, Lesser Antilles: Contamination in the arc crust. J. Geol. Soc. Lond. 141, 427-445.

567 Thirlwall, M.F., Graham, A.M., Arculus, R.J., Harmon, R.S., Macpherson, C.G., 1996.  
 568 Resolution of the effects of crustal contamination, sediment subduction, and fluid transport

in island arc magmas: Pb-Sr-Nd-O isotope geochemistry of Grenada, Lesser Antilles.  
Geochim. Cosmochim. Acta 60, 4785-4810.

Toothill, J., Williams, C.A., Macdonald, R., Turner, S.P., Roger, N.W., Hawkesworth, C.J.,  
Jerram, D.A., Ottley, C.J., and Tindle, A.G., 2007. A complex petrogenesis for an arc  
magmatic suite, St Kitts, Lesser Antilles. J. Petrology 48, 3-42.

Valley, J.W., Kitchen, N., Kohn, M.J., Niendorf, C.R., Spicuzza, 1995. UWG-2, a garnet  
standard for oxygen isotope ratios: Strategies for high precision and accuracy with laser  
heating. Geochim. Cosmochim. Acta 59, 5223-5231.

Van Soest, M.C., Hilton, D.R., Macpherson, C.G., Matthey, D.P., 2002. Resolving sediment  
subduction and crustal contamination in the Lesser Antilles arc: a combined He-O-Sr  
Isotope approach. J. Petrology 43, 143-170.

White, W.M., Dupré, B., 1986. Sediment Subduction and Magma Genesis in the Lesser  
Antilles: Isotopic and Trace Element Constraints. J. Geophys. Res. 91, 5927-5941.

Yogodzinsky, G.M., Kelemen, P.B., 1998. Slab melting in the Aleutians: implications of  
an ion probe study of clinopyroxene in primitive adakite and basalt. Earth Planet. Sci. Lett.  
158, 53-65.

Ysaccis, R., 1997. Tertiary evolution of the northeastern Venezuela offshore. Ph.D. thesis,  
Rice University, Houston. 285 pp.

**Figure captions**

Figure 1: Bathymetric map of the Lesser Antilles arc showing the islands, the trench-deformation front, the main ridges, the Grenada and Tobago basins and the locations of Deep Sea Drilling Project (DSDP) hole 543/543A and hole 144. Figure modified from Van Soest et al. (2002).

Figure 2: Whole rock compositions of St Lucia lavas. (a) Sr and Nd and (b) Pb and Nd isotopic diversity. St Lucia data show a similar range to most of the Lesser Antilles arc, ranging between typical oceanic arc compositions and Atlantic sediments cored at the front of the trench (DSDP sites 144 and 543; Carpentier et al., 2008, 2009). SVC = Soufriere Volcanic Complex. Pre-SVC lavas with typical oceanic arc compositions, called Pre-SVC1, are shown by open circles and lavas with the most radiogenic compositions, called Pre-SVC2, are represented by striped circles. The SVC lavas are shown by solid red circles. (b)  $^{87}\text{Sr}/^{86}\text{Sr}$  and (d)  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $\text{SiO}_2$  (wt. %) of St Lucia lavas showing the two trends observed.  $\text{SiO}_2$  and Sr-Nd-Pb isotopic compositions are provided in the Table 1. Tonga, South Sandwich, Mariana and Aleutian compositions from Georock database: <http://georoc.mpch-mainz.gwdg.de/georoc/>. MORB field is mid-Atlantic Ridge between  $30^\circ\text{N}$  and  $30^\circ\text{S}$  (data from PETDB: <http://petdb.org/science.jsp/>) and the Lesser Antilles arc field represents data from other islands: Grenada from Thirlwall and Graham (1984); Soufrière, St Vincent from Heath et al. (1998); Dominica and Martinique from Davidson (1986, 1987) and Davidson and Wilson (2011); Mt Misery, St Kitts from Toothill et al. (2007), The Quill, Statia from Davidson and Wilson (2011); Saba from Sherman (1992).

Figure 3:  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios of twenty plagioclase phenocrysts showing isotopic disequilibrium among four of the most contaminated SVC lavas. The whole rock value for

613 each lava is shown as a horizontal line. For all data, 2 standard errors (SE) are  $< 0.000014$   
614 which is smaller than the symbol size. Data are presented in Table 2.

615 Figure 4:  $\delta^{18}\text{O}$  values of phenocrysts from SVC and Pre-SVC lavas (symbols as in Fig.2).  
616 Plag = plagioclase; Qz = quartz, Py = pyroxene; Am = amphibole and MA = mantle range.  
617 Mantle ranges are from Bindeman and Valley (2002) for Quartz (from differentiation of  
618 mantle derived magma), Chazot et al. (1997) for pyroxene and amphibole and Eiler et al.  
619 (2000) for plagioclase (defined using crystals from samples with  $\text{SiO}_2$  similar to Pre-SVC  
620 mafic lavas). 2 sd reproducibility error of the O isotope technique was typically  $\pm 0.4 \text{ ‰}$   
621 (see section 3.3).

622 Figure 5: Correlation between mineral  $\delta^{18}\text{O}$  and whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\text{SiO}_2$  (symbols as  
623 in Fig. 2). (a,b) plagioclase and pyroxene  $\delta^{18}\text{O}$  vs. whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$ . (c,d) plagioclase  
624 and pyroxene  $\delta^{18}\text{O}$  vs. whole rock  $\text{SiO}_2$ . Mixing models between mantle ( $\delta^{18}\text{O} = +5.7 \text{ ‰}$ )  
625 and sediment with  $\delta^{18}\text{O}$  of  $+20 \text{ ‰}$  (1) and  $+35 \text{ ‰}$  (2) are also shown. Oxygen concentration  
626 is assumed to be the same for both the mantle and the sediment in the model. MA = MORB  
627 mantle range with  $\delta^{18}\text{O}$  from Eiler et al. (2000) and  $^{87}\text{Sr}/^{86}\text{Sr}$  from mid-Atlantic Ridge  
628 between  $30^\circ\text{N}$  and  $30^\circ\text{S}$  (data from PETDB: <http://petdb.org/science.jsp/>). In the schematic  
629 inset  $[\text{Sr}]_C$  is the Sr concentration in sediment and  $[\text{Sr}]_M$  is the Sr concentration in the  
630 mantle during source contamination (SC) and in the melt during crustal assimilation (CA).

631 Figure 6: Variation of  $\text{SiO}_2$  and  $\text{CaO}$  with  $\text{MgO}$  composition with the Pre-SVC and SVC  
632 lavas. Upper continental crust composition is from Rudnick and Fountain (1995). The  
633 schematic inset illustrates the impact of incorporation of large amounts of terrigenous

634 sediment into the mantle source on primitive magma compositions. The same concept can  
635 be applied to CaO versus MgO, for large amounts of carbonate rich sediment.

636 Figure 7: Schematic model for the St Lucia magmatic plumbing system through time to  
637 explain the Pre-SVC and SVC whole rock and mineral isotopic compositions. The bottom  
638 panel illustrates the storage, intrusion and eruption of the Pre-SVC lavas. The magma  
639 storage is limited and/or occurs mostly in the mantle and in the oceanic crust: assimilation  
640 of sediment (purple) is limited. The middle panel illustrates the development of a large  
641 SVC andesitic complex at shallower depth where active assimilation of sediment takes  
642 place. Finally, the upper panel illustrates the evolution of the SVC dacite from the andesite.  
643 Minimal or no assimilation occurs at this stage.



Fig. 1

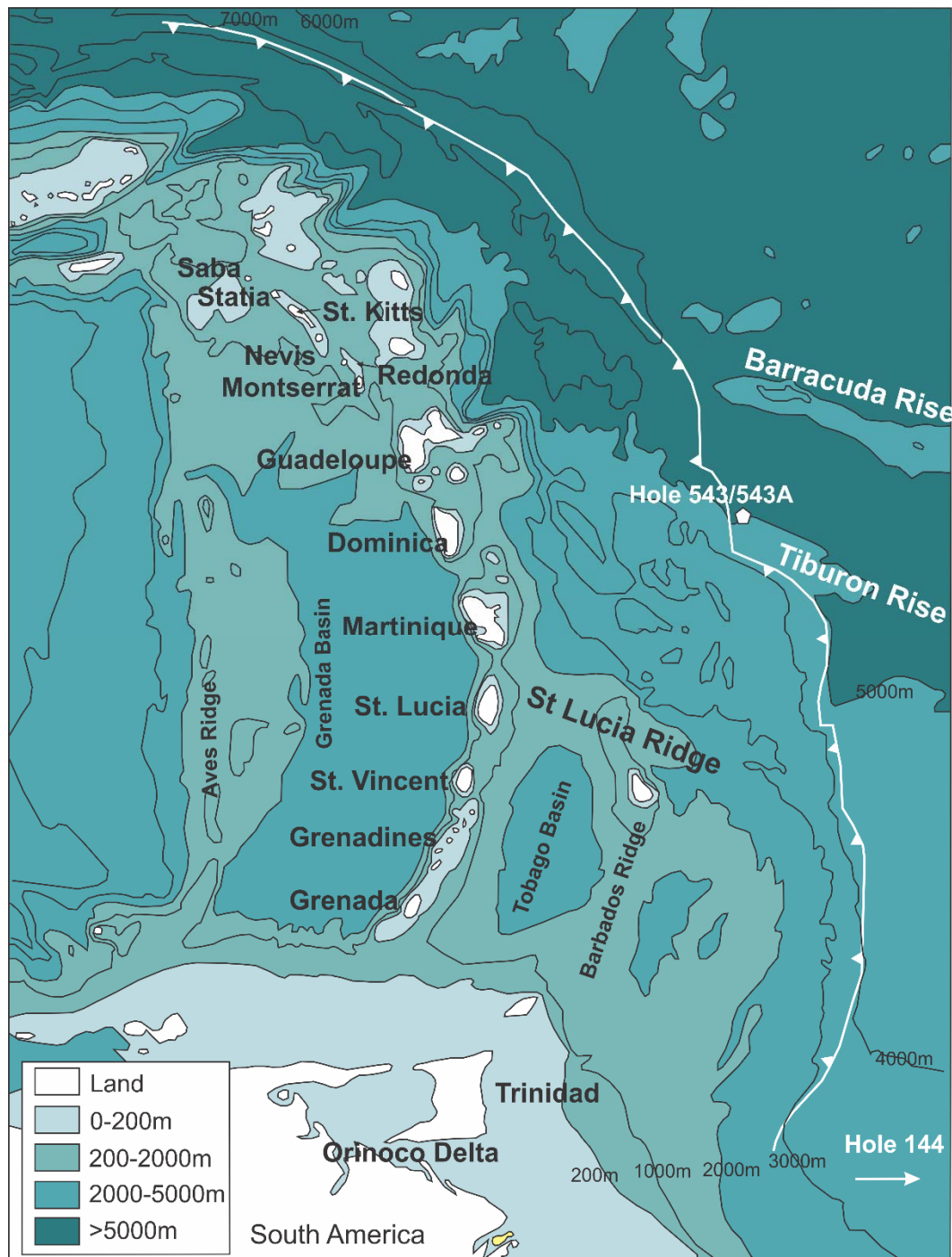


Fig. 2

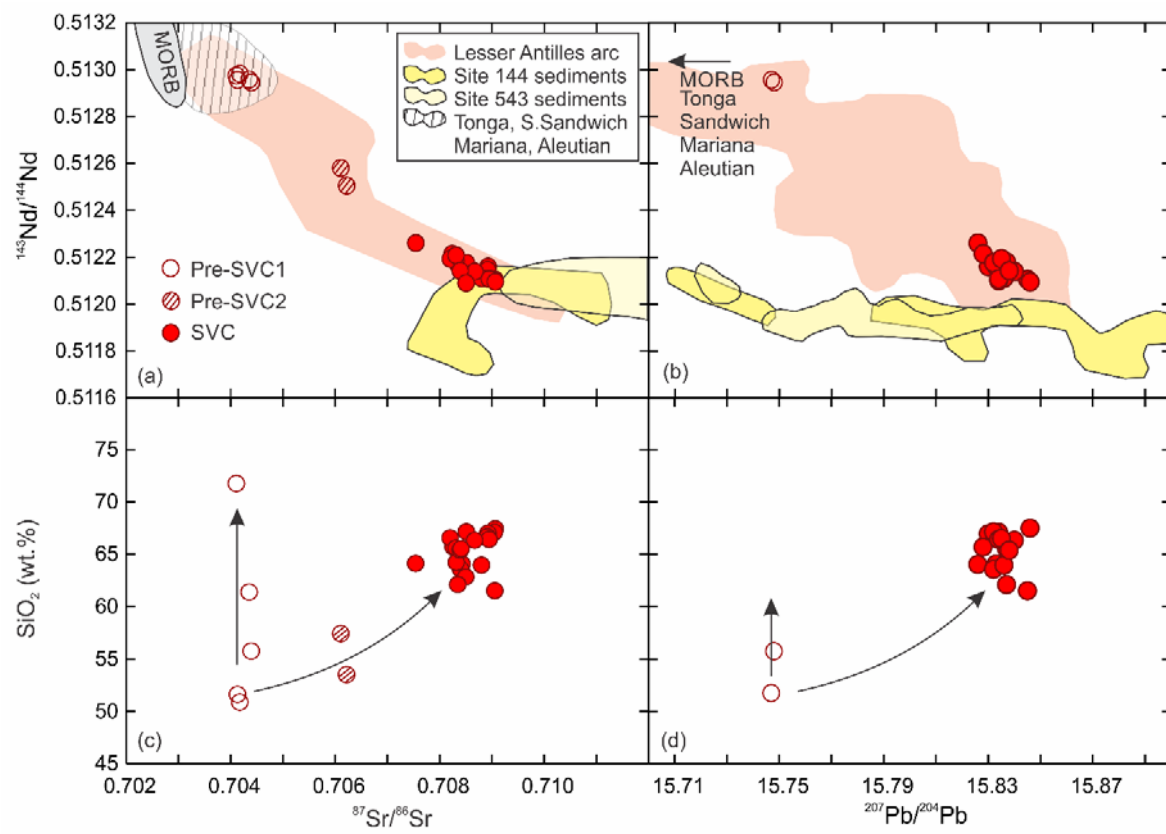


Fig. 3

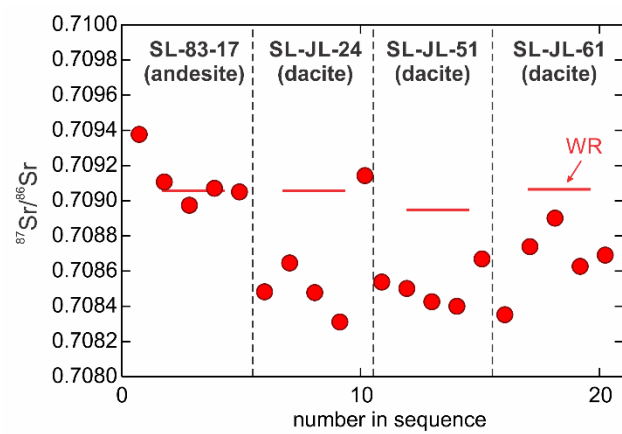


Fig. 4

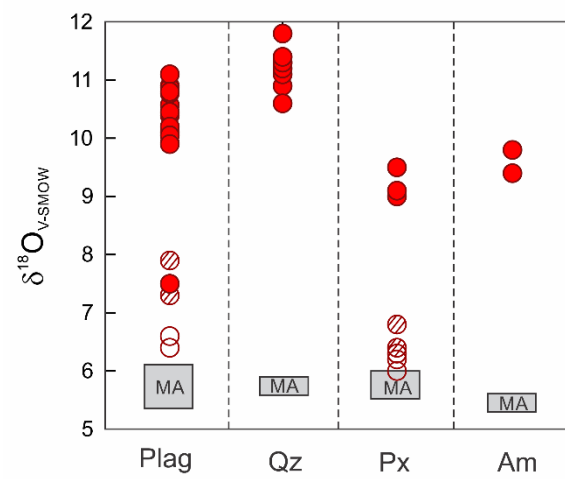


Fig. 5

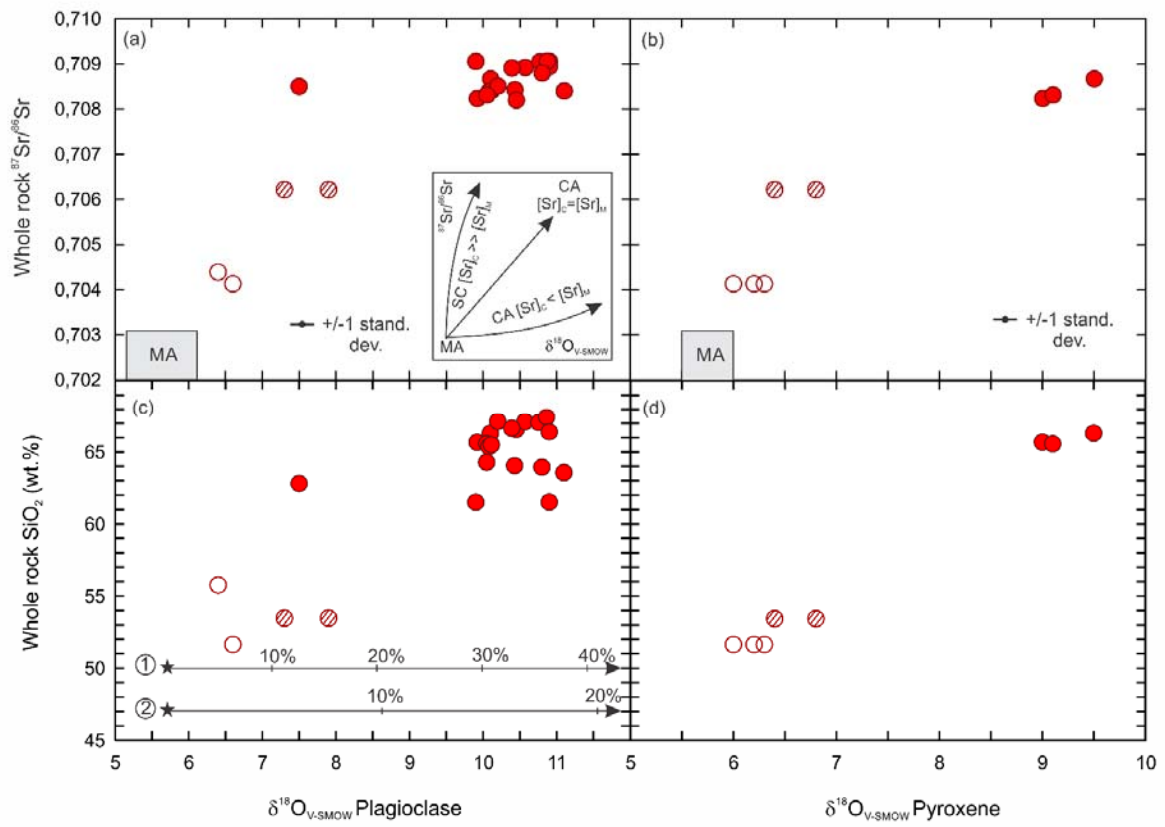


Fig. 6

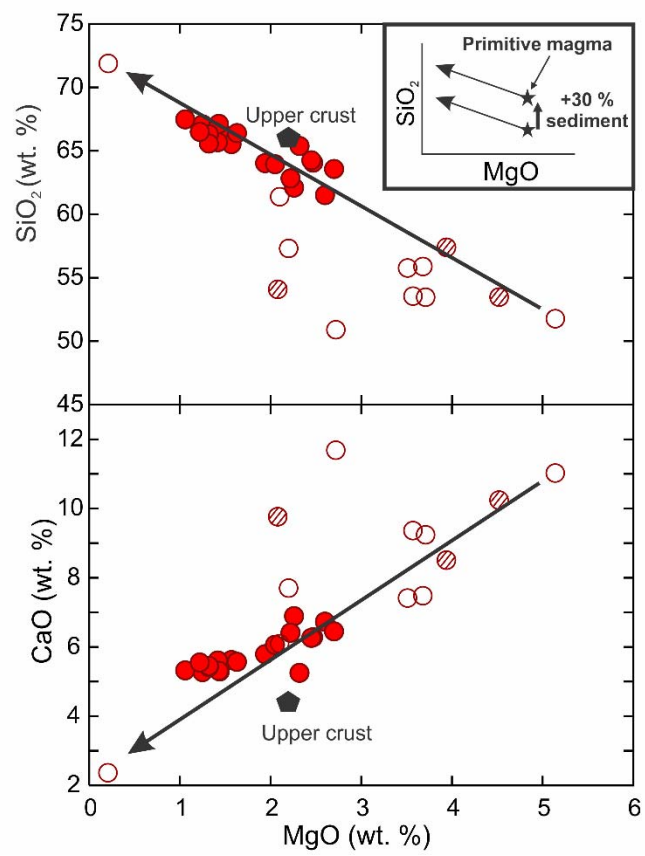
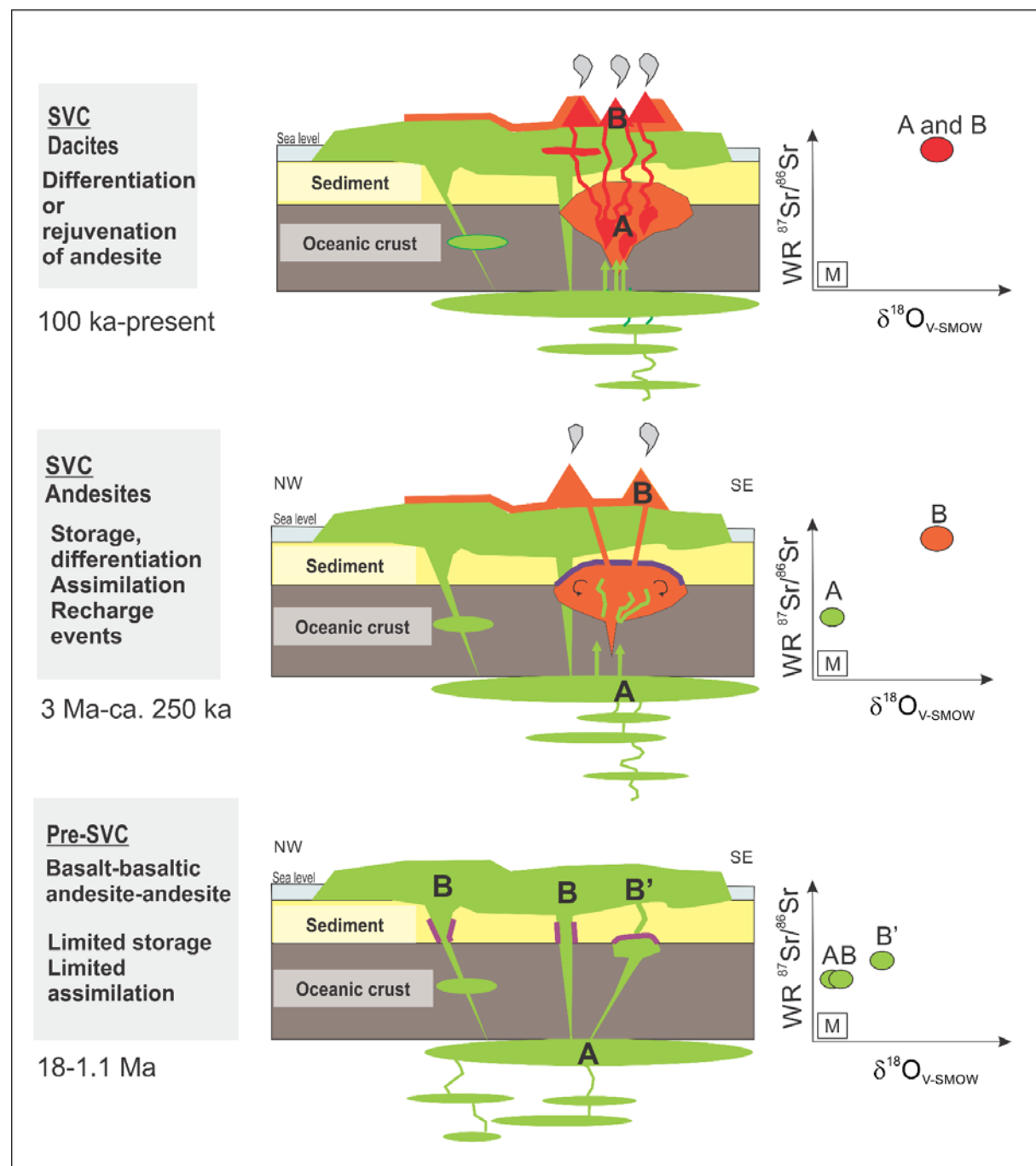


Fig. 7



**Table 1: St Lucia whole rock Sr-Nd-Pb isotopic compositions and the corresponding SiO<sub>2</sub> and CaO content in wt.%. SiO<sub>2</sub> and CaO concentrations are from Davidson (1987) and Lindsay et al. (2013), and normalised to 100% volatile free.**

Durham University							
Sample name	<sup>143</sup> Nd/ <sup>144</sup> Nd	<sup>87</sup> Sr/ <sup>86</sup> Sr	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb	SiO <sub>2</sub>	CaO
SL8303	0.512261	0.707542	19.728	15.826	39.438	64	5.79
SL8308	0.512161	0.708925	19.721	15.830	39.457	66.9	5.36
SL8312	0.512147	0.708914	-	-	-	66.7	5.29
SL8315	0.512169	0.708346	19.760	15.837	39.467	62.1	6.89
SL8316	0.512161	0.70843	19.737	15.833	39.466	64.1	6.28
SL8317	0.512106	0.709056	19.797	15.845	39.489	61.5	6.73
SL8319	0.51218	0.708412	19.748	15.837	39.479	65.5	5.62
SL8324	0.512215	0.708237	19.730	15.828	39.446	65.7	5.61
SL8325	0.512946	0.704394	19.291	15.748	38.930	55.8	7.41
SL8344	0.512957	0.704132	19.341	15.747	39.110	51.8	11.02
SL-JL-22	0.512178	0.708402	19.753	15.832	39.471	63.6	6.45
SL-JL-23	0.512111	0.708801	19.779	15.836	39.479	63.9	6.06
SL-JL-24	0.512101	0.709049	19.770	15.834	39.484	67.1	5.27
SL-JL-33	0.512177	0.708511	19.759	15.832	39.473	67.1	5.31
SL-JL-51	0.512108	0.708946	19.766	15.834	39.484	66.4	5.57
SL-JL-57	0.51214	0.708672	19.773	15.840	39.489	66.3	5.42
SL-JL-61	0.512096	0.709063	19.782	15.846	39.528	67.5	5.32
SL-JL-79	0.512187	0.708313	-	-	-	65.6	5.45
SL-JL-83	0.512194	0.708202	19.758	15.835	39.483	66.5	5.55
SL-JL-84	0.512209	0.708313	-	-	-	64.3	6.26
Macquarie University							
Sample name	<sup>143</sup> Nd/ <sup>144</sup> Nd	<sup>87</sup> Sr/ <sup>86</sup> Sr	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb	SiO <sub>2</sub>	CaO
SL8326	0.512505	0.706219	-	-	-	53.5	10.24
SL8339	0.51258	0.706106	-	-	-	57.4	8.53
SL8341	0.512958	0.704354	-	-	-	61.4	6.09
SL8342	0.512983	0.704174	-	-	-	50.9	11.68
SL8345	0.512975	0.704109	-	-	-	71.9	2.37
SL-JL-1	0.512143	0.708393	19.757	15.838	39.489	65.4	5.25
SL-JL-2	0.512091	0.708504	-	-	-	62.8	6.41

**Table 2:  $^{87}\text{Sr}/^{86}\text{Sr}$  of single plagioclase grains separated from four of the most continental-like SVC hand samples. Whole rock  $\text{SiO}_2$  (wt. %) and  $^{87}\text{Sr}/^{86}\text{Sr}$  are also shown (see Table 1 for references).**

Sample name	$^{87}\text{Sr}/^{86}\text{Sr}$	2 SE	Whole rock $^{87}\text{Sr}/^{86}\text{Sr}$	Whole rock $\text{SiO}_2$
SL8317PI1	0.709377	0.000010	0.709056	61.5
SL8317PI2	0.709107	0.000009		
SL8317PI3	0.708974	0.000013		
SL8317PI4	0.709071	0.000009		
SL8317PI5	0.709050	0.000008		
SL-JL-24PI6	0.708482	0.000006	0.709049	67.1
SL-JL-24PI7	0.708646	0.000005		
SL-JL-24PI8	0.708478	0.000010		
SL-JL-24PI9	0.708311	0.000007		
SL-JL-24PI10	0.709143	0.000009		
SL-JL-51PI11	0.708538	0.000007	0.708946	66.4
SL-JL-51PI12	0.708501	0.000010		
SL-JL-51PI13	0.708426	0.000007		
SL-JL-51PI14	0.708400	0.000007		
SL-JL-51PI15	0.708669	0.000005		
SL-JL-61PI16	0.708352	0.000008	0.709063	67.5
SL-JL-61PI17	0.708739	0.000006		
SL-JL-61PI18	0.708901	0.000007		
SL-JL-61PI19	0.708627	0.000007		
SL-JL-61PI20	0.708691	0.000006		



**Table 3:  $\delta^{18}\text{O}$  of single mineral separates from St Lucia along with the corresponding whole rock  $\text{SiO}_2$  (wt.%) and Sr isotopic composition. WR = whole rock.  $\text{SiO}_2$  content from Davidson (1987) and Lindsay et al. (2013) and normalised to 100% volatile free.**

Sample name	Kind of mineral	Group	$\delta^{18}\text{O}_{\text{V-SMOW}} (\text{‰})$	WR $\text{SiO}_2$	WR $^{87}\text{Sr}/^{86}\text{Sr}$
8308PI	Plagioclase	SVC	10.6	66.9	0.708925
8312PI	Plagioclase	SVC	10.4	66.7	0.708914
8316PI	Plagioclase	SVC	10.4	64.1	0.70843
8317PI	Plagioclase	SVC	10.9	61.5	0.709056
8317PI	Plagioclase	SVC	9.9	61.5	0.709056
8319PI	Plagioclase	SVC	10.1	65.5	0.708412
8324PI	Plagioclase	SVC	9.9	65.7	0.708237
8325PI	Plagioclase	Pre-SVC1	6.4	55.8	0.704394
8326PI1	Plagioclase	Pre-SVC2	7.3	53.5	0.706219
8326PI2	Plagioclase	Pre-SVC2	7.9	53.5	0.706219
8344PI	Plagioclase	Pre-SVC1	6.6	51.8	0.704132
JL01PI	Plagioclase	SVC	10.1	65.4	0.708393
JL02PI	Plagioclase	SVC	7.5	62.8	0.708504
JL22PI	Plagioclase	SVC	11.1	63.6	0.708402
JL23PI	Plagioclase	SVC	10.8	63.9	0.708801
JL24PI	Plagioclase	SVC	10.8	67.1	0.709049
JL33PI	Plagioclase	SVC	10.2	67.1	0.708511
JL51PI	Plagioclase	SVC	10.9	66.4	0.708946
JL57PI	Plagioclase	SVC	10.1	66.3	0.708672
JL61PI	Plagioclase	SVC	10.9	67.5	0.709063
JL83PI	Plagioclase	SVC	10.5	66.5	0.708202
JL84PI	Plagioclase	SVC	10.0	64.3	0.708313
JL79PI	Plagioclase	SVC	10.0	65.6	0.708313
8303Qz	Quartz	SVC	11.2	64.0	0.707542
JL01Qz	Quartz	SVC	11.3	65.4	0.708393
JL02Qz	Quartz	SVC	11.4	62.8	0.708504
JL22Qz	Quartz	SVC	11.3	63.6	0.708402
JL23Qz	Quartz	SVC	10.9	63.9	0.708801
JL24Qz	Quartz	SVC	11.4	67.1	0.709049
JL33Qz	Quartz	SVC	11.1	67.1	0.708511
JL51Qz	Quartz	SVC	11.3	66.4	0.708946
JL57Qz	Quartz	SVC	10.6	66.3	0.708672
JL61Qz	Quartz	SVC	11.8	67.5	0.709063
8324Opx	Orthopyroxene	SVC	9	65.7	0.708237
8326Py1	Clinopyroxene	Pre-SVC2	6.8	53.5	0.706219
8326Py2	Clinopyroxene	Pre-SVC2	6.4	53.5	0.706219
8344Py1	Clinopyroxene	Pre-SVC1	6.0	51.8	0.704132
8344Py2	Clinopyroxene	Pre-SVC1	6.2	51.8	0.704132
8344Py3	Clinopyroxene	Pre-SVC1	6.3	51.8	0.704132
JL57Opx	Orthopyroxene	SVC	9.5	66.3	0.708672
JL79Opx	Orthopyroxene	SVC	9.1	65.6	0.708313
8308Am	Amphibole	SVC	9.8	66.9	0.708925
JL33Am	Amphibole	SVC	9.4	67.1	0.708511